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ARAGONITE FRACTION DATING OF VERMETIDS IN THE CONTEXT OF PALEO SEA-LEVEL CURVES RECONSTRUCTION

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ABSTRACT. Identifying and tackling recrystallization is a critical factor in the reliable radiocarbon (^{14}C) dating of carbonates, since exogenous carbon can be incorporated and thus mask the real age of the samples. Vermetids are among the most important bioindicators used for paleo sea-level reconstruction, and the accuracy of their chronology can significantly impact sea-level curves. Age differences larger than 1 ^{14}C kyr before and after acid etching, combined with X-ray diffraction (XRD) analysis that indicates a significant amount of calcite still remains in the shell, led us to apply the previously developed carbonate density separation protocol (CarDS). Using a solution of sodium polytungstate, with density of 2.80 g/cm^3, we successfully separated different carbonate fractions for a set of 10 vermetid samples from the coast of Rio de Janeiro, southeast of Brazil. Each separation was verified by XRD analysis and the ^{14}C concentrations of different fractions were compared. The results show that the calcite fraction in the studied vermetid samples varied from 12 to 63% and aragonite fraction ages are up to 2 ^{14}C kyr older than the raw samples, thus confirming the efficacy of CarDS in removing young carbonates and the importance of density separation to vermetids prior to accelerator mass spectrometry (AMS) dating.

KEYWORDS: CarDS, recrystallization, sample preparation, sodium polytungstate.

INTRODUCTION

An essential tool for studies on coastal evolution during the Quaternary is the reconstruction of relative paleo-sea levels through space-time indicators (Strachan et al. 2014). For the construction of precise and accurate curves, it is necessary to establish large and reliable datasets (Baker and Haworth 2000; Martin et al. 2003; Leorri et al. 2013). Relative sea level variations may be studied through geological (beach rocks and marine abrasion terrace), archaeological (shell mounds) and biological proxies (fossil vermitids and barnacle incrustation) (Laborel and Laborel-Deguen 2005; Pirazzoli 2005; Edwards et al. 2013). These indicators can be divided in two categories: the simple, which provide space and time information when associated to a dating method, enabling the determination of mean paleo-sea levels, and the compound, which need to be associated to other indicators, since they only provide a rough estimate of past sea level (Pirazzoli 2005; Angulo and de Souza 2014). Dating charcoal and shells from archaeological sites, for example, requires additional information that relates the depositional environment to its relation to the sea level (Pluet and Pirazzoli 1991; Kelletat 2006; Angulo and de Souza 2014).

Among the most used indicators are the fossil vermetids. Since they live in a narrow range within the mean tide, they provide precise information on the relative sea level. Their structure generally comprises high magnesium calcite (HMC), low magnesium calcite (LMC), and aragonite. Following Burton and Walter (1987), LMC and HMC are defined as a calcite that has <5 mol% and 5–20 mol% of $MgCO_3$ respectively. Living individuals are mostly constituted of aragonite and HMC, most likely biogenic calcite. All three

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*Corresponding author. Email: kitamacario@gmail.com polymorphs have the same $CaCO_3$ chemical composition with differences in the crystalline lattice. Such material is susceptible to diagenesis and depending on the environmental conditions a rearrangement of the crystalline structure may take place. Aragonite and HMC tend to dissolve and recrystallize into the more stable LMC form (secondary calcite). During this process, Ca^{2+} cations exchange position as CO_3^{2-} anions rotate, causing an increase of ca. 8% in volume (Bathurst 1972). Several factors can influence the process and most of them depend on the chemistry of the fluid containing the fossil (Morse et al. 1997). Kinetic and biological factors can also interfere (Douka et al. 2010).

Fyfe and Bischoff (1965) and Taft (1967) studied the transformation of aragonite into calcite in aqueous media and reported patterns of thermodynamical parameters during the reaction. Diagenesis is a matter of great concern for the scientific community as exogenous carbon may become included in the crystal structure and in the case of radiocarbon (^{14}C) dating, incorporation of recent carbon may affect the age determination. The standard method for carbonate samples preparation consists in removing the external layer of the sample by means of acid etching or sandblasting. Screening techniques such as the use of Fiegl solution (Friedman 1959; Brock et al. 2010), X-ray diffraction (XRD) (Douka et al. 2010) or FTIR (Loftus et al. 2015) to detect the presence of calcite have been used to evaluate the extent of recrystallization and also the effectiveness of pretreatment prior to accelerator mass spectrometry (AMS) dating.

A previous pilot study (Jesus et al. 2017), which aimed to reconstruct sea-level curves in Brazil, found that ^{14}C ages of samples before and after acid etching were up to 1 ^{14}C kyr different. Moreover, the sample structure indicated that for some samples the acid etching was ineffective in the removal of secondary calcite. Considering that the age difference was already large, these results were discarded as they would affect the sea-level curve due to the lack of accuracy in age determination.

IMPACT OF INACCURATE DATING ON SEA-LEVEL CURVES: AN EXAMPLE

In order to demonstrate the importance of accuracy of vermetid ^{14}C dates and potential impact on sea-level curves reconstructions, we have built hypothetical depth/time curves for contaminated and uncontaminated vermetids. In Figure 1, the curve (solid red line) resembles the accepted sea-level variation pattern, with sea-level rise up to 5 kBP followed by decrease to present level (Jesus et al. 2017). In this example, we assume recrystallization was minimum and the standard chemical pretreatment with HCl etching would be sufficient to remove calcite from all samples. The best fit for this curve would be a 5th degree polynomial representing the rise in sea-level up to 2.5 m above the present level with a decrease after 4.5 kBP.

Considering an alternative scenario where two samples have 50% of calcite formed due to recrystallization and assuming 1 kBP for the average age of such contamination, the result would be apparent ages of more than 2 ^{14}C kyr younger. This shift in the ages of two samples would result in a very different curve, with oscillations in the mean sea-level around 3 kBP. It is important to notice that a curve derived from empirical data would be based on calibrated ages and the larger the dataset the lesser it would be affected by a shift in two points. Inaccuracy in ^{14}C dates due to inadequate removal of contaminants could be responsible for the interpretation of oscillations in sea-level during the Holocene, which have resulted in a significant point of disagreement between researchers.

Two different interpretations stem from the work of Suguio et al. (1985), Angulo et al. (2002) and Jesus et al. (2017). After the last progressive maximum around 5 kBP, sea level would

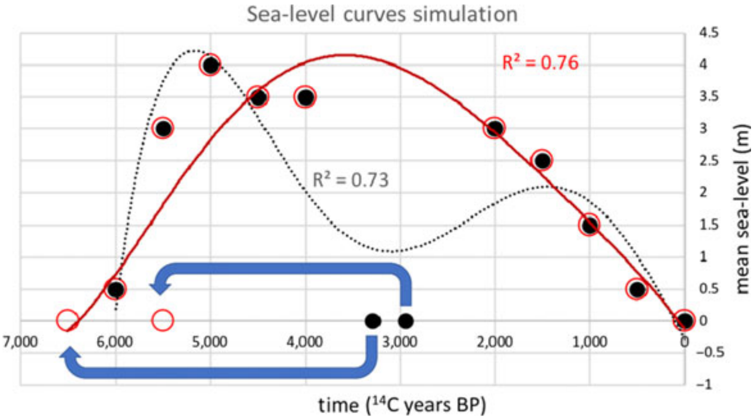

Figure 1 Hypothetical paleo-sea level curves. Assuming two vermetid samples with 50% contamination with average 1 kBP old calcite (dashed black line) and assuming real vermetid age (solid red line). Blue arrows indicate changes in ^{14}C ages of contaminated samples. (Please see electronic version for color figures.)

either have (a) gently decreased until present day (Angulo et al. 2002; Jesus et al. 2017), or (b) decreased but with oscillations between 3 and 2 kBP (Suguio et al.1985).

This question affects the morphogenetic evolution of coastal plains and influences archaeological and paleontological research, as well as many other disciplines. A few equivocal results have already been noticed in literature that may compromise the construction of sea-level curves (Castro et al. 2014). These include (1) mistaken age determination of the samples forming the curves, (2) lack of clarity in the interpretation of geological data in relation to paleo-sea levels, and (3) inappropriate calibration of ^{14}C data.

Changes in the results caused by the underestimation of ages may result in equivocal interpretations of the reconstructed paleoenvironment for a given region. According to Walker and James (1992), a set of sedimentary facies follow sea-level variations in response to both transgressions and regressions. Of course, other parameters can influence the sedimentary record, such as the sedimentary rates (Suguio 1999), coastal declivity and waves (Psuty 1988) but sea-level variations are responsible for the majority of coastal transformations. Figure 2 shows possible changes in coastal morphology, which can be evaluated from the two resulting sea-level curves (Figure 1). In Figure 2b, where the difference in sea level exceeds 2.5 m, there is a significant impact to coastal and lowland areas. Coastal dynamics and processes that impact the coastal line may further increase the magnitude of any possible environmental alteration.

Up to now, XRD has been used to evaluate the degree of recrystallization in vermetids and samples are discarded when replacement calcite is within the shells (Yates 1986). Considering the importance of accurately dating vermetids and the inefficiency of the standard sample preparation protocols to remove secondary calcite, we decided to investigate the use of density separation methods in this context. Douka et al. (2010) developed a protocol (CarDS) based on a known density liquid to separate recrystallized from original fractions of a sample, resulting in a demonstrably age estimation for carbonate samples subjected to diagenesis. In this paper, we analyze 10 vermetid samples collected on islands on the coast of Rio de

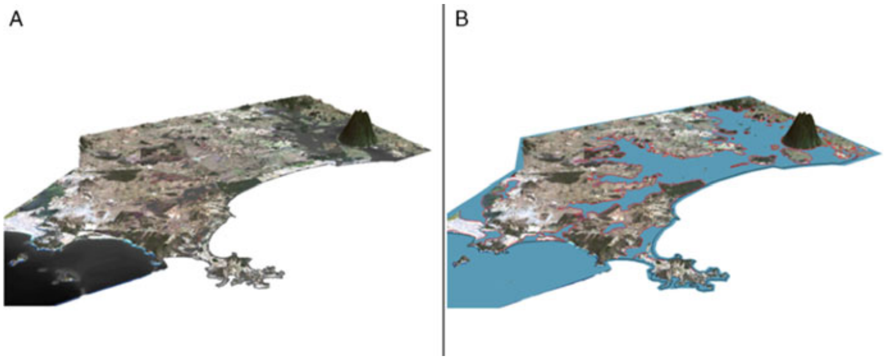

Figure 2 Coast of Rio de Janeiro. Simulation of possible coastal flooding at 3 kBP based on the two hypothetical curves in Figure 1. Sea level 0.5 m above present value (A) and 2.5 m above present value (B).

Janeiro with the aim of comparing the routine (acid etching) and CarDS preparation protocols and evaluating the impact of these different protocols on sea-level reconstructions.

METHODS

Sampling

Vermetid samples were collected in two different locations: eight from Ilha Grande Bay and two from Armação de Búzios (Figure 3). Fossil vermetid incrustations can be found in breaches of coastal rocks, protected from the waves action and above the present sea-level (Figure 4).

Sample preparation was performed at the radiocarbon laboratory of the Fluminense Federal University (LAC-UFF). In order to evaluate the fraction of preserved aragonite and the recrystallized calcite, samples were crushed in a mortar and pestle (grain size less than 150 μm) and were analyzed using an XRD. Part of the powdered sample was pretreated with hydrogen peroxide (H_2O_2) to remove any organic fraction. We added 5 mL of 30% H_2O_2 with heat (60°C), repeating the process once every 2 hr or until no more gas was evolved.

Overall, 10 samples were divided in five different subsamples: (1) untreated sample (bulk raw); (2) after 50% etching with HCl 0.1 M (bulk HCl); (3) bulk after H_2O_2 (bulk H_2O_2); (4) aragonite fraction (separated from bulk H_2O_2 by density); and (5) calcite fraction (separated from bulk H_2O_2 by density).

Density Separation

The CarDS protocol uses a heavy liquid (in our case sodium polytungstate, SPT) of known density to separate original aragonitic structures from secondary calcite ones, prior to AMS dating. The powder SPT was weighed and added to ultrapure water, dissolved with the aid of a magnetic agitator. The density was measured with a digital densimeter and approximately 300 mL of 2.80 g/cm^3 solution was prepared. 300 mg of sample was weighed in a 15-mL falcon tube and 5 mL of SPT solution was added. The mixture was blended using a vortex for 30 s then sonicated for 10 min at room temperature and finally centrifuged for 15 min at 3000 rpm. This resulted in separation of two phases, a supernatant floating phase and a pellet at the bottom of the tube. With care, not to accidentally mix the separated phases, we froze

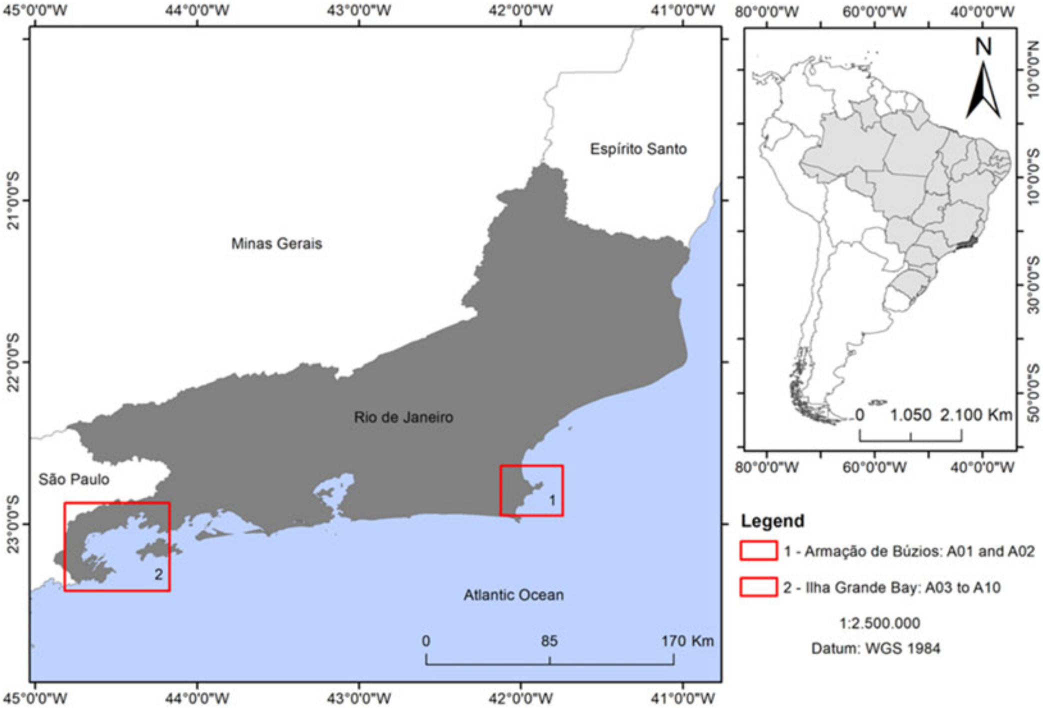

Figure 3 Sampling location on the coast of Rio de Janeiro. Samples A01 and A02 were collected in Armação de Buzios (1) and samples A03-A10 were collected in Ilha Grande Bay.

Figure 4 Vermetids on coastal rock at Ilha Grande Bay.

the bottom part with liquid nitrogen and removed the supernatant with a Pasteur pipette, while slowly adding water. Again, we added 5 mL of SPT solution and repeated the separation process. Finally, we added 5 mL of ultrapure water, vortexed for 30 s, centrifuged for 10 min at 3000 rpm and removed the supernatant with pipette. This step was repeated two more times to ensure the total removal of SPT residues. Additionally, the supernatant was kept and washed with water to remove SPT residues. The final samples were frozen for 24 hours and lyophilized for 48 hr. After separation, both phases were in the form of a fine powder.

X-Ray Diffraction Analysis

Both separated phases and bulk samples were analyzed using XRD. Sample preparation and analysis were undertaken at the Laboratório de Difração de Raios X of the Fluminense Federal University (LDRX – UFF). A Bruker AXS 84 D8 Advance (Cu Kα radiation, 40 kV, 40 mA) model was operated in a Bragg–Brentano θ/θ 85 configuration, with the diffraction patterns being collected in a flat geometry with steps of 0.02 degrees and accumulation time of 2.0 s per step using a PSD detector (Bruker AXS LynexEye model). The XRD data were refined following the Rietveld method with the GSAS-II software (Toby and Von Dreele 2013).

Accelerator Mass Spectrometry

Bulk samples and subsamples were chemically treated to extract carbon dioxide and were then converted to graphite. Solid samples were placed in vials with septum covers and were connected to a vacuum system pumped out through a needle. 1.0 mL phosphoric acid was injected into evacuated tubes with a gastight syringe and left overnight at room temperature to hydrolysis reaction to occur. The tubes were connected back to the line and the gas was transferred in order to be purified. Dry ice/ethanol traps were used to remove water from samples while liquid nitrogen was used to trap the CO_2 so that non-condensable gases could be removed. CO_2 samples were then transferred to 9-mm Pyrex tubes for graphitization. These tubes were previously prepared with titanium hydride and zinc on the bottom and iron powder inside a 6-mm inner tube. Tubes were sealed with an oxy-acetylene torch and heated to 550ºC for 7 hr so that CO_2 could be reduced to graphite (Xu et al. 2007; Macario et al. 2015, 2017). Graphite samples were pressed in aluminum cathodes and their ^{14}C concentration was measured at the Center for Applied Isotopes Studies at the University of Georgia (samples A01, A02 and A10) or at the NEC SSAMS system of the Fluminense Federal University (samples A03–A09). Information on the UGA and the UFF systems are reported elsewhere (Cherkinsky et al. 2010 and Linares et al. 2015, respectively).

RESULTS AND DISCUSSION

For the subsamples that underwent H_2O_2 treatment we compared the weight before and after pretreatment to estimate the amount of organic matter (OM) in the samples. The results are shown in Table 1. These values are approximations only as there is always some loss of carbonate powder during the treatment and transferring of samples.

In order to validate the density separation method for the vermetid samples, we evaluate the crystallographic features of all subsamples. Figure 5 displays the X-ray diffractograms for sample A10, before and after density separation. On the top, A10 (bulk H_2O_2) shows the high percentage of calcite indicating strong recrystallization of the original aragonitic structure and on the bottom, A10_CSPT shows the presence of HMC, which is part of the original composition of non fossil shell samples (Lowenstam and Weiner 1989) and insignificant concentration of LMC, the stable form of calcium carbonate (Jamieson 1953). The X-ray diffractograms for all other samples are presented in Figure 6.

As shown in Table 2, the extraction of calcite by density separation was successful. It should be noticed that the XRD method is semi-quantitative, the proportion being estimated in comparison

Table 1 Estimate of organic matter % in each sample based on weight before and after H_2O_2 treatment.

Sample	Initial weight (mg)	Final weight (mg)	Organic matter %
A01	1754.1	1461.3	16.7
A02	1121.4	954.2	14.9
A03	1259.5	981.3	22.1
A04	1357.3	997.5	26.5
A05	985.5	872.6	11.5
A06	1253.3	1004.8	19.8
A07	873.8	689.9	21.0
A08	1592.7	1378.9	13.4
A09	1136.7	909.7	20.0
A10	852.2	722.7	15.2

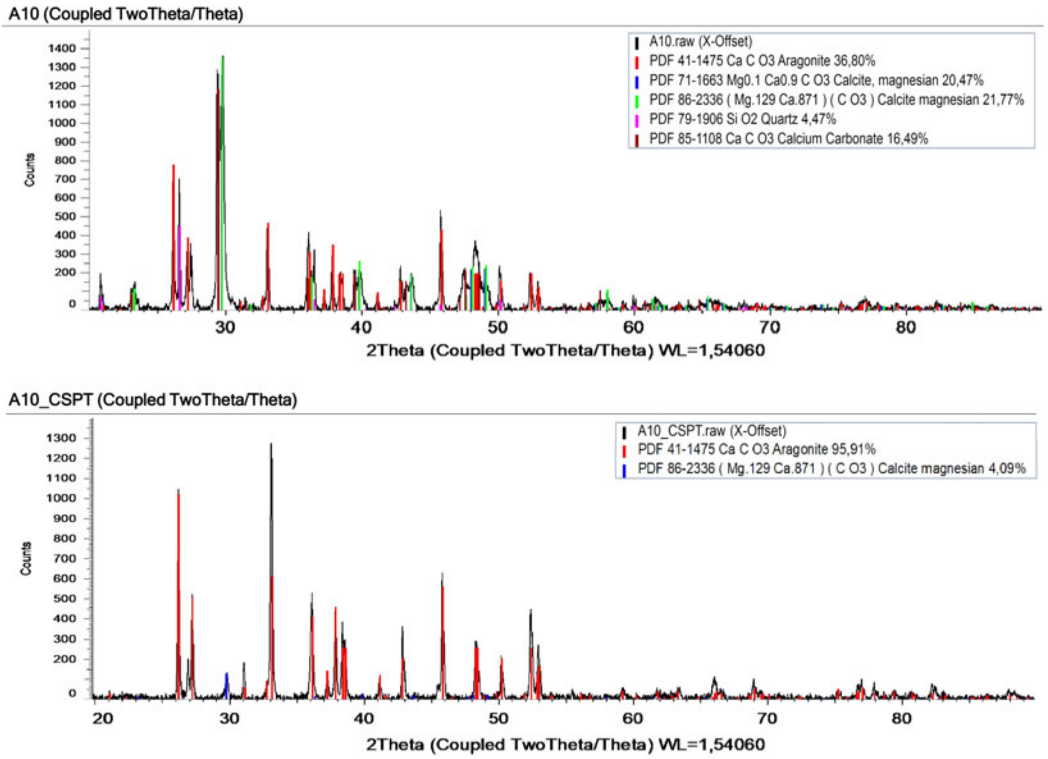

Figure 5 X-ray diffractograms of sample A10 before SPT (top) and after SPT (bottom).

to a reference standard. However, the obtained precision in the percent rates is enough to demonstrate decrease (samples A07 and A10) or total removal of the calcite peaks (Figure 6).

Accelerator Mass Spectrometry

The AMS results for vermetids samples with different chemical treatments are shown in Table 3 and Figure 7.

Table 2 Percentages of the aragonite and calcite fractions in the different samples.

	Before		After	
Sample	Aragonite (%)	Total calcite (%)	Aragonite (%)	Total calcite (%)
A01	45.83	54.27	100.00	0.00
A02	43.55	56.58	100.00	0.00
A03	47.30	50.97	100.00	0.00
A04	64.32	30.39	100.00	0.00
A05	73.27	21.47	100.00	0.00
A06	83.39	12.14	100.00	0.00
A07	34.47	62,93	93.94	6.06
A08	62.57	26.01	100.00	0.00
A09	76.74	13.22	100.00	0.00
A10	36.80	58.73	96.46	3.54

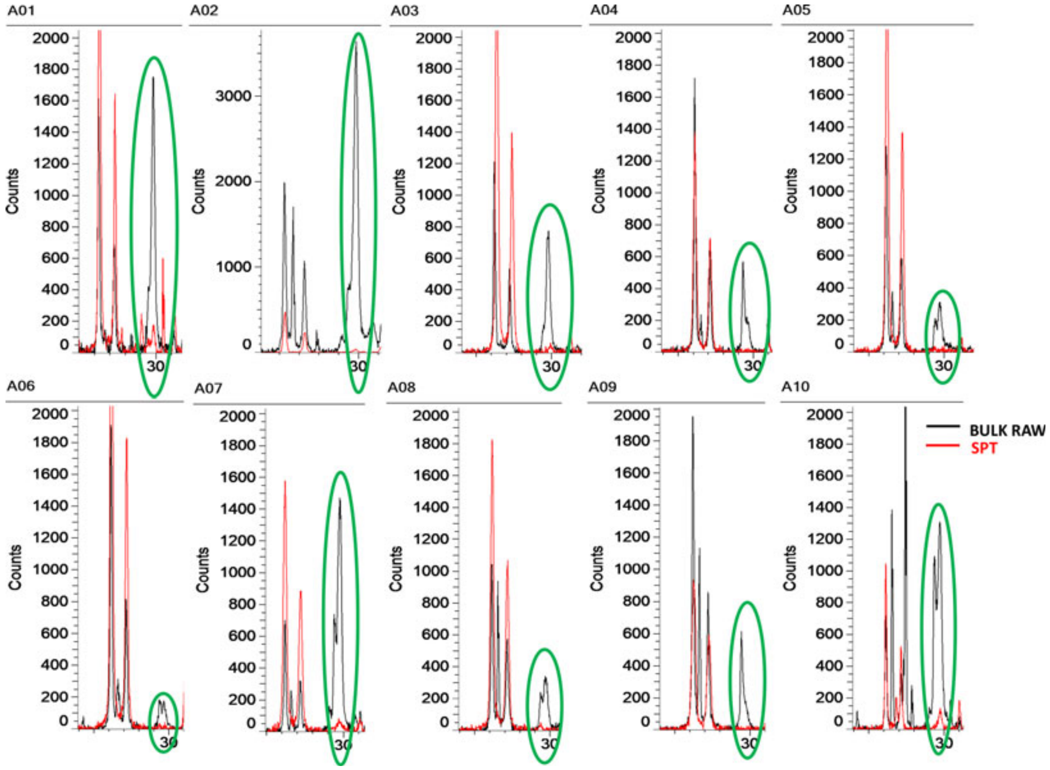

Figure 6 X-ray diffractogram showing removal of calcite (circled in green) for the 10 samples. In black the untreated sample, in red the sample after pretreatment with CarDS.

Comparison of results (Table 3) between bulk H_2O_2 and bulk HCl (50% etching with 0.1 M HCl) treatments for each sample shows a significant discrepancy in ages in most cases. This indicates the presence of surface contamination that the etching protocol manages to remove. These contaminants could originate from recrystallized calcite, encrustation with

Table 3 Results of AMS analysis at the University of Georgia (UGA lab codes) or at the Fluminense Federal University (LACUFF lab codes). The aragonite and calcite fractions are obtained after treatment with the CarDS protocol.

Sample	Treatment	^{14}C age (BP)	Discrepancy from aragonite fraction	UGA ID	LACUFF ID
A01	Bulk raw	3658 ± 38	31%	–	190334
	Bulk HCl	4205 ± 45	20%	–	190335
	Bulk H_2O_2	3564 ± 29	33%	32489	–
	Aragonite	5285 ± 29	–	32491	–
	Calcite	3707 ± 27	30%	32492	–
A02	Bulk raw	3381 ± 32	30%	34701	–
	Bulk HCl	3016 ± 29	37%	34703	–
	Bulk H_2O_2	4031 ± 31	16%	32490	–
	Aragonite	4822 ± 30	–	32493	–
	Calcite	4189 ± 28	13%	32494	–
A03	Bulk raw	1053 ± 32	37%	–	180175
	Bulk HCl	1425 ± 73	15%	–	180176
	Bulk H_2O_2	–	–	–	–
	Aragonite	1677 ± 36	–	–	180177
	Calcite	1321 ± 36	21%	–	190193
A04	Bulk raw	786 ± 40	10%	–	180178
	Bulk HCl	927 ± 52	–6%	–	180179
	Bulk H_2O_2	–	–	–	–
	Aragonite	877 ± 47	–	–	180180
	Calcite	509 ± 33	42%	–	190194
A05	Bulk raw	1709 ± 32	0%	–	180181
	Bulk HCl	1822 ± 38	–7%	–	180182
	Bulk H_2O_2	1450 ± 33	15%	–	190196
	Aragonite	1702 ± 47	–	–	180183
	Calcite	1450 ± 31	15%	–	190195
A06	Bulk raw	873 ± 31	5%	–	180184
	Bulk HCl	940 ± 50	–3%	–	180185
	Bulk H_2O_2	817 ± 27	11%	–	190198
	Aragonite	917 ± 31	–	–	180186
	Calcite	785 ± 31	14%	–	190197
A07	Bulk raw	3527 ± 49	39%	–	180187
	Bulk HCl	3587 ± 51	38%	–	180188
	Bulk H_2O_2	–	–	–	–
	Aragonite	5819 ± 45	–	–	180189
	Calcite	5108 ± 37	12%	–	190199
A08	Bulk raw	1682 ± 36	40%	–	180190
	Bulk HCl	2222 ± 41	21%	–	180191
	Bulk H_2O_2	2451 ± 34	13%	–	190201
	Aragonite	2814 ± 40	–	–	180192
	Calcite	2391 ± 33	15%	–	190200
A09	Bulk raw	962 ± 41	–29%	–	180193
	Bulk HCl	1092 ± 60	–47%	–	180194
	Bulk H_2O_2	753 ± 31	–1%	–	190203
	Aragonite	743 ± 34	–	–	180195
	Calcite	774 ± 30	–4%	–	190202

Table 3 (*Continued*)

Sample	Treatment	^{14}C age (BP)	Discrepancy from aragonite fraction	UGA ID	LACUFF ID
A10	Bulk raw	3198 ± 24	16%	30648	–
	Bulk HCl	3256 ± 24	14%	30649	–
	Bulk H_2O_2	3600 ± 32	5%	34702	–
	Aragonite	3792 ± 25	–	30650	–
	Calcite	3632 ± 26	4%	30651	–

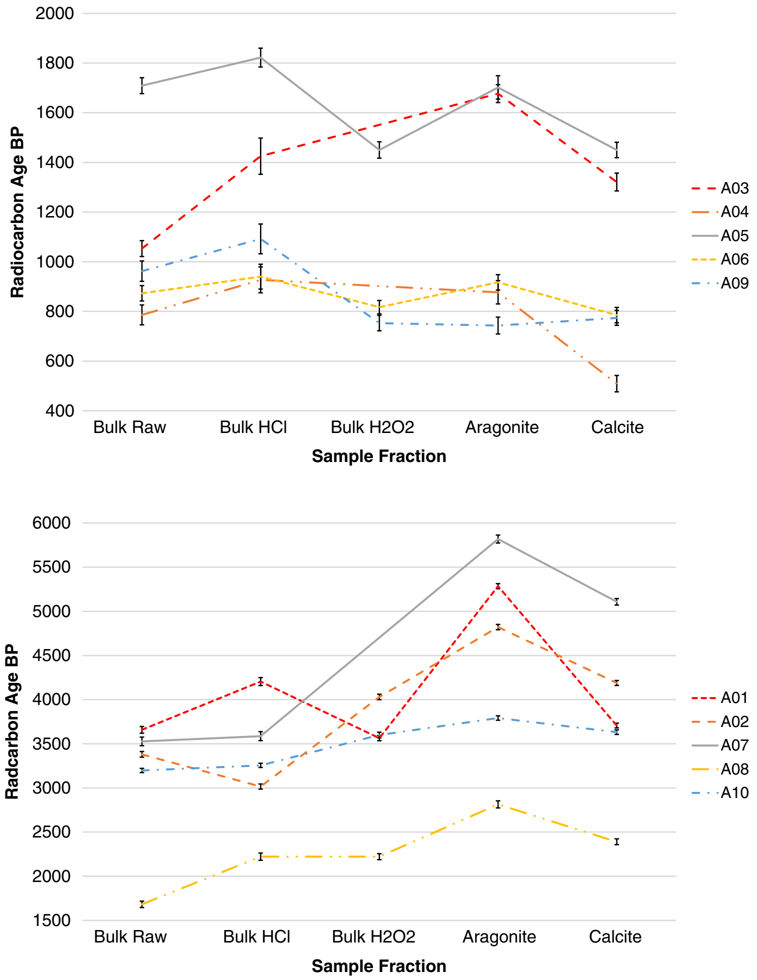

Figure 7 ^{14}C ages obtained from each chemical fraction for vermetid samples with aragonite fraction older than 2 kBP (bottom) and younger than 2 kBP (top).

Table 4 Protocol originally described by Douka et al. (2010) and the one used in the present work.

Douka et al. (2010)	This work
Mechanical cleaning	Mechanical cleaning
• Air-abrasive system	• Scalpel
Organics removal	Organics removal
• Vacuum at 250ºC and 350ºC	• Hydrogen peroxide
CarDS	CarDS-V
• Lithium heteropolytungstate (LST)	• Sodium polytungstate (SPT)
• 100 mg of sample	• 300 mg of sample
• 4–5 mL of LST	• 5–6 mL of SPT
• Centrifugation for 20 min at 3500 rpm	• Centrifugation for 15 min at 3000 rpm
• First density of solution 2.75 g/cm^3 and second with 2.83 g/cm^3	• Same density, 2.80 g/cm^3 for the two steps
• Carbonate residue was frozen for 12 hr and freeze-dried for 24 hr	• Carbonate residue was frozen for 24 hr and freeze-dried for 48 hr

other organisms, or any material that could have accumulated to the surface of the shell. Physical pretreatment includes removing any visible contamination prior to chemical treatment. However, vermetids have internal surfaces which are not accessible. In the standard etching protocol, we assume that it is more likely that carbon contamination is caused by recrystallization on the external surface of the sample. This protocol, however, does not remove organic material, visible in some samples that have lime residue on the surface, which is also observed on the diffractograms. Therefore, samples followed to organic matter oxidation by means of H_2O_2 treatment.

In some cases, however, the XRD result revealed a slight increase in the calcite concentration of samples treated with H_2O_2 (Bulk H_2O_2), and the ^{14}C analysis of this fraction also resulted in slightly younger ages when compared to ages on bulk samples. This contamination may be related to partial dissolution of the oldest carbonate fraction during H_2O_2 treatment as its pH was about 3.

In the cases where aragonite and calcite were separated using CarDS, we see that in most cases the aragonite fraction yielded older ages compared to the Bulk H_2O_2 sample. Notwithstanding, although the age shift is not in itself an indication of the right age, the method we describe above has proved to be efficient in removing contamination of carbonate samples and crucial for obtaining more reliable dates of vermetids.

Comparison of Methods

Table 4 shows the differences between the protocol originally described by Douka et al. (2010) and the one we used in the current work. The differences include the initial preparation of samples, and the use of a single solution of SPT with density of 2.80 g/cm^3 in this work.

In the present work, we report complete separation of calcite for samples with up to 57% recrystallization. Above this concentration, remaining calcite was observed (Table 2) and repetition of the separation could not be performed as there was no more sample available.

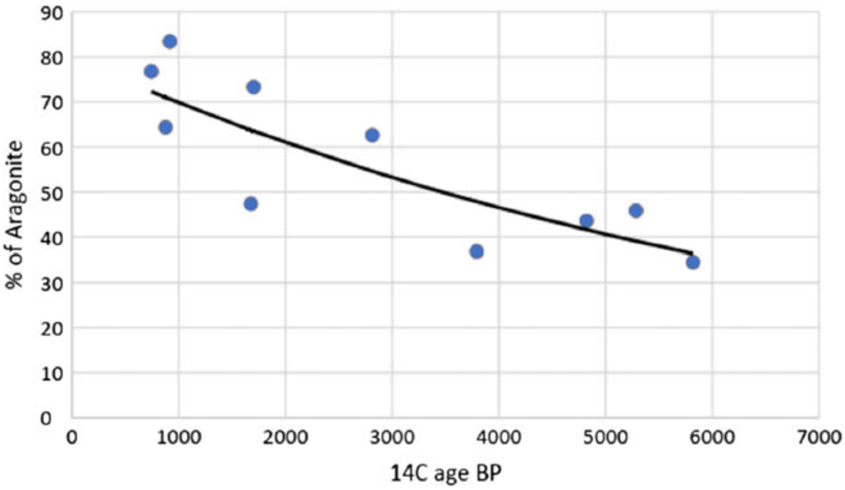

Figure 8 Percent of original aragonite against the ^{14}C age of the aragonite fraction.

The ^{14}C results show significant differences in more than half of the samples, indicating the importance of the application of such protocol to vermetid samples prior to AMS dating. In particular, for samples older than 3 kBP, with calcite contents over 50% (Figure 8), the impact of contamination through the incorporation of exogenous carbon during recrystallization was very relevant.

CONCLUSIONS

The impact of crystallization in the case of vermetid AMS dating has been understudied, yet its effect in the construction of past sea-level curves, is detrimental. Here, we successfully separate primary and secondary carbonate fractions of vermetid shells using a density protocol further verified by XRD analysis. Both aragonite and calcite fractions were directly dated, allowing us to evaluate the extent of contamination in each shell. Comparison of the ^{14}C concentrations of raw (untreated) fractions and fractions treated with our routine protocol shows that the aragonite fraction can be up to 2 ^{14}C kyr older than the untreated sample, thus confirming the efficacy of CarDS and the importance of density separation to vermetids prior to AMS dating. We hope that this work demonstrates the need for a more efficient way of identifying and limiting the issue of secondary contamination of shells prior to AMS dating and special care with sample preparation prior to sea-level reconstructions.

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